

Self-avoiding knots

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Scaling arguments are used to analyze the size of topologically constrained closed ring polymer with excluded volume. It is found that there exists a finite range of polymer thickness (excluded volume) in which self-avoidance is unimportant and polymer swelling compared to the Gaussian size is entirely due to the topological constraints.

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The ability to knot is the most obvious and the least understood property of long strings, such as ropes, threads, spaghetti, flux lines, or polymers. Knots in DNA have been directly observed [1, 2]. The compelling, albeit circumstantial, proof of their importance can be seen in the fact that Nature had undertaken to design special cell machinery (called topological enzymes) spending energy to simplify DNA topology [3]. Knots and other topological constraints are also of great importance in equilibrium and dynamics properties of polymer materials, such as melts, gels, networks, etc. Despite this ample motivation, current understanding of polymer topology is very limited.

Apart from mathematical theory of knot invariants [4], the study of knots in polymers was dominated for a long time by computer simulations [5, 6, 7, 8]. The incorporation of sophisticated topological invariants to compute entropy of the topologically constrained polymers remains a difficult challenge [9]. More recently, some insights into the statistical properties of knots were developed based on various scaling arguments [10, 11, 12, 13, 14, 15]. As in other cases in soft condensed matter physics [16, 17], scaling is the theory of choice where more sophisticated approaches are too difficult.

The simplest question of polymer physics is that about the size (say, root-mean-squared gyration radius) of a single macromolecule in a dilute solution. In general, this question is not understood for the topologically constrained polymer ring. As a first step in this direction, it was recently shown [12] (confirming the earlier conjecture [18]) that topological constraints in the knot effectively lead to self-avoidance on the large enough length scales. As a result, the size of a polymer ring with the topology of a trivial knot (an unknot) scales as $R \sim \ell N^\nu$ even for the polymer with negligible excluded volume. Here, N is the number of effective segments, ℓ is the segment length, and $\nu \approx 0.588 \approx 3/5$ is the well known critical exponent of self-avoiding walks [16]. This result has been also extended for the non-trivial knots using the aspect ratio of maximally inflated tube, p , as a topological invariant [10]. Overall, the result of the work [12] reads

$$R \simeq \begin{cases} \ell N^{1/2} p^{-1/6} & \text{when } N < pN_{00} \\ \ell N^\nu p^{-\nu+1/3} N_{00}^{-\nu+1/2} & \text{when } N > pN_{00} \end{cases} . \quad (1)$$

Here, N_{00} is the characteristic length of knotting; it comes from the observation [6, 7] and mathematical proof [22] that the probability to have an unknot in a phantom chain (which freely crosses itself) goes like $e^{-N/N_{00}}$. Numerically, $N_{00} \approx 300$ [6, 7]. Thus, the theory predicts that $R \sim N^{3/5}$, if N is large enough, independently of the knot type. This prediction was scrutinized using computer simulations [19, 20, 21]; the most recent work [21] claims complete agreement with the predicted scaling.

In this paper, our goal is to study the interplay of topological constraints and excluded volume interactions - two factors both of which are inevitably present in any real polymer. We imagine a polymer ring of N effective segments of the length ℓ and diameter d each. We would like to emphasize that end closing itself would not change the polymer size scaling, affecting only a numerical prefactor. This means, if we imagine a ring with excluded volume, but phantom (for which all topological classes of conformations are available, like in the presence of topological enzyme [23]), then the usual prediction [16] holds:

$$R_g \sim \begin{cases} \ell N^{1/2} & \text{when } N < 1/r^2 \\ \ell N^\nu r^{2\nu-1} & \text{when } N > 1/r^2 \end{cases} . \quad (2)$$

Thus, our goal if to generalize together the Eqs. (1) and (2). Our results are summarized by the Fig. 1, in which the diagram of scaling regimes is presented in terms of variables N and $r = d/\ell$. The paper is organized around the discussion of this diagram.

As an important input of our analysis, we shall rely on the following insight gained by computer experiments [24, 25] regarding the probability of knotting for the excluded volume polymer. As one might have guessed, excluded volume enhances the probability of a trivial knot, somewhat suppressing all non-trivial knots. What is much more difficult to guess is that the probability of a trivial knot remains exponential in N , with characteristic length very sharply depending on the excluded volume parameter. According to [24, 25],

$$\begin{aligned} p_{\text{unknot}}(N, r) &\simeq \exp[-N/N_0(r)] , \\ N_0(r) &\simeq N_{00} \exp[\beta r^\nu] , \\ N_{00} &\approx 300 , \beta \approx 30 , \nu \approx 1 . \end{aligned} \quad (3)$$

In fact, the authors of the work [25] found that according to their numerical data, the value of ν is slightly below

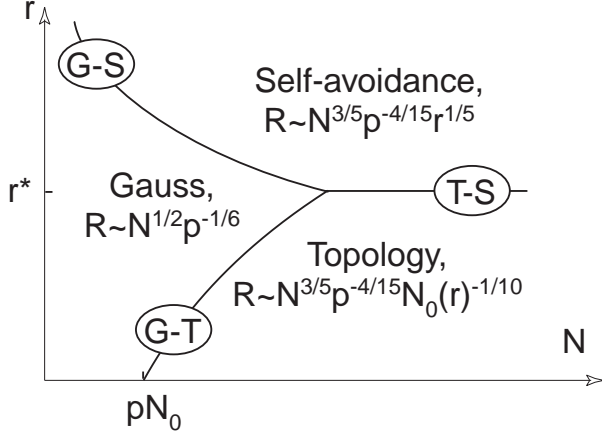


FIG. 1: Diagram of scaling regimes of a polymer ring. N is the number of effective segments in the chain, r is the dimensionless thickness of the polymer (the ratio of the diameter to the segment length), p is the knot invariant - diameter to the length ratio of maximally inflated tube [10]. The scaling of polymer size for every regime is indicated in the figure using the approximate value of the critical exponent $\nu \approx 3/5$. The cross-over boundaries are as follows: the $G - S$ line between Gaussian and self-avoidance regimes $r^2 \simeq p/N$; the $G - T$ line between Gaussian and topological regimes $N \simeq pN_0(r)$ (see Eq. (3)); and the $T - S$ line between topological and self-avoidance regimes $r = r^* \approx 0.03$.

unity, $\nu \approx 0.85$. They also claimed that the coefficient A may depend on the model. Neither of these details is important for our purposes here, we will only use the fact that the characteristic length of knotting, $N_0(r)$ is sharply increasing with r .

We are now in a position to start discussing the scaling diagram, Fig. 1. Let us begin with a trivial knot, or an unknot, in which case p (in the scaling sense) is of order unity ($p = 2\pi$).

First of all, there is obviously a regime when neither excluded volume nor topological constraints are important. This range is labeled as Gaussian in Fig. 1, because chain size in this regime scales as that of a Gaussian polymer, $R \sim N^{1/2}$. This happens if the conditions $N < 1/r^2$ (2) and $N < N_0(r)$ (3) are met simultaneously. In particular, the latter condition, according to the formula (3) ensures that even for the phantom chain the part of conformation space corresponding to all non-trivial knots is very small; therefore, set of conformations of phantom chain is practically the same as that of a trivial knot.

When we cross over the $G - S$ boundary $N \simeq 1/r^2$, excluded volume effect takes over, but topological constraints may still remain unimportant if $N < N_0(r)$. In this regime, labeled as dominated by self-avoidance in Fig. 1, chain size is given by $R \simeq \ell N^\nu r^{2\nu-1}$.

Another regime is obtained from Gaussian if we cross over the $N = N_0(r)$ line $G - T$, remaining at $N < 1/r^2$. In this case, we should imagine the chain as consist-

ing of $N/N_0(r)$ blobs, of $N_0(r)$ monomers each. Inside each blob, as its length is smaller than the characteristic knotting length, the topological constraints are insignificant, as well as the excluded volume; therefore, the blob size is about $R_{\text{blob}} \simeq \ell N_0(r)^{1/2}$. On the other hand, the chain of blobs is topologically constrained, and, therefore, according to [12], we get for the chain size $R \simeq R_{\text{blob}} (N/N_0(r))^\nu \simeq \ell N^\nu N_0(r)^{-\nu+1/2}$.

At this stage, it is useful to check the self-consistency of our result. As we know [10, 12], the trivial knot size results from the balancing of two entropic factors. On the one hand, chain has entropic elasticity $\sim R^2/N\ell^2$ which resists swelling. On the other hand, topologically constrained blobs resist interpenetration. At the equilibrium R , both entropic contributions are of the same order. We must now check that the second virial term corresponding to the excluded volume interactions is smaller than either of the above mentioned terms. Given that the second virial coefficient of elongated (rod-like) segments is about $\ell^2 d$, the self-consistency condition reads

$$\ell^2 d \frac{N^2}{R^3} < \frac{R^2}{\ell^2 N}. \quad (4)$$

Note, that this condition is equivalent to $R > R_{\text{Flory}}$, where $R_{\text{Flory}} \simeq \ell N^{3/5} r^{1/5}$ is the Flory estimate of polymer size without topological constraints [16]. Thus, this condition means simply that excluded volume is unimportant if the chain swells more for topological reasons than it would due to the excluded volume. Simple algebra indicates that this condition is met if $N_0(r) < 1/r^2$, which is equivalent to $r < r^*$. Numerically, according to eq. (3), $r^* \approx 0.03$.

Finally, let us see what happens if $N_0(r) > 1/r^2$ and $N > N_0(r)$. Diagram Fig. 1 indicates that in this case we cross over the $T - S$ boundary and enter again the same self-avoidance regime which we discussed previously in terms of crossing over the $G - S$ line. Let us show why this is indeed the same regime. We should imagine once again that our chain consists of $N/N_0(r)$ blobs, with $N_0(r)$ monomers in each blob. In the present case, since $N_0(r) > 1/r^2$, excluded volume is important for each blob, so that the blob size is about $R_{\text{blob}} \simeq \ell N_0(r)^\nu r^{2\nu-1}$. Since the chain of blobs is topologically constrained, overall chain size scales as $R \simeq R_{\text{blob}} (N/N_0(r))^\nu \simeq \ell N^\nu r^{2\nu-1}$, which does not involve the topological quantity of $N_0(r)$ and coincides with our result for the self-avoidance dominated regime.

This completes the analysis for the case of an unknot (trivial knot).

Let us now consider some non-trivial knot, characterized by the length-to-diameter ratio of maximally inflated tube, also called ideal knot representation. The specific values of p for many knots were computed by Pieranskii et al [26]. Following the ideology of [10, 12], we imagine the polymer as confined in the maximally inflated tube such that it is unknotted inside the tube. This corre-

sponds to viewing the polymer as consisting of p roughly spherical blobs, with N/p monomers in each blob. Furthermore, since the tube is maximally inflated, the blobs fill completely (in the scaling sense) the entire volume of the coil, which means $R^3 \simeq pR_{\text{blob}}^3$, or

$$R \simeq p^{1/3} R_{\text{blob}}. \quad (5)$$

Therefore, all we have to do is to address all possible regimes of the chain inside the blob.

The simplest case is when neither excluded volume nor topology are of importance inside the blob. This happens when both $N/p < 1/r^2$, which is below the $G-S$ line in Fig. 1, and $N/p < N_0(r)$, which is above or to the left of the $G-T$ line. In this regime every blob is Gaussian, yielding $R_{\text{blob}} \simeq \ell(N/p)^{1/2}$ and, according to formula (5),

$$R \simeq \ell N^{1/2} p^{-1/6}, \text{ when } N < p/r^2 \text{ and } N < pN_0(r). \quad (6)$$

This is Gaussian regime of Fig. 1.

When N/p exceeds $1/r^2$, we cross over the $G-S$ line into the regime dominated by self-avoidance. In this case, the blob size is about $R_{\text{blob}} \simeq \ell(N/p)^\nu r^{2\nu-1}$. Therefore, formula (5) yields

$$R \simeq \ell N^\nu p^{-\nu+1/3} r^{2\nu-1}, \text{ when } N > p/r^2 \text{ and } r > r^*. \quad (7)$$

Similar to the case of the trivial knot, this regime, which we call self-avoidance dominated, is valid all the way from the $G-S$ boundary $N \simeq p/r^2$ to the $T-S$ boundary $r = r^*$.

Finally, if r is small, but the blob length N/p exceeds $N_0(r)$, then blobs become topologically constrained. This means, it becomes important that the chain inside the tube is unknotted, and so must be every blob. In this regime, blob size scales as $R_{\text{blob}} \simeq \ell(N/p)^\nu N_0(r)^{-\nu+1/2}$. Plugging this into formula (5) leads to

$$R \simeq \ell N^\nu p^{-\nu+1/3} N_0(r)^{-\nu+1/2}, \text{ when } N > pN_0(r) \text{ and } r < r^*. \quad (8)$$

This is topology dominated regime.

It is instructive to summarize the results by looking at the ratio of the given knot size R to the size of a phantom ring polymer (2), with the same length N , segment length ℓ , and excluded volume r :

$$\xi = \frac{R_{\text{knot}}(p)}{R_{\text{phantom}}}. \quad (9)$$

This quantity is useful, because R_{phantom} can be also understood as the average size over all knot types, and such quantity can be easily extracted from computer simulations data [19, 20]. Various regimes for this quantity are

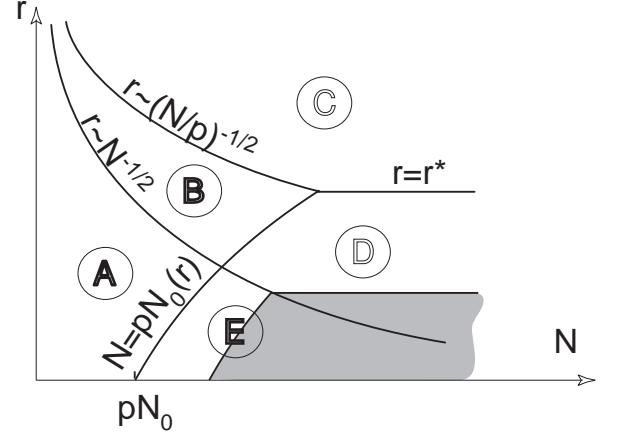


FIG. 2: Scaling regimes for the quantity ξ (9). As in Fig. 1, the results are shown using the approximate value of the critical exponent $\nu \approx 3/5$. Regime A: both topologically constrained and phantom chains are Gaussian, $\xi \simeq p^{-1/6} < 1$. Regime B: phantom polymer swells due to excluded volume, while knot remains Gaussian: $\xi \simeq p^{-1/6} (Nr^2)^{-1/10} < 1$. Regime C: both phantom polymer and the knot swell due to the excluded volume, $\xi \simeq p^{-4/15} < 1$. Regime D: knot swells because of topology, while phantom ring swells due to the excluded volume, $\xi \simeq p^{-4/15} (N_0(r)r^2)^{-1/10}$. Regime E: knot is swollen due to the topological constraint, while phantom ring is Gaussian, $\xi \simeq p^{-4/15} (N/N_0(r))^{1/10}$. In the shaded area, which includes parts of the regimes D and E, the topologically constrained polymer is more expanded than the phantom (averaged of all knots).

outlined in the Fig. 2, where the cross-over lines of the scaling diagram Fig. 1 are superimposed with the line $r \simeq 1/\sqrt{N}$ separating Gaussian and swollen regimes for the phantom polymer.

Somewhat counterintuitive result is that there is a parameter range (shaded in Fig. 2) in which topologically constrained knot is more expanded than phantom average over all knots. This happens because for the phantom chain (with annealed topological disorder) in this range more complex knots (with p larger than the given value) are prevailing, they are more compact, and they dominate the average R_{phantom} . This result is at least qualitatively in agreement with the simulation data [19].

Metzler et al [13, 14] recently reexamined the possibility of "knot segregation," which was briefly discussed at the end of [10] and later analyzed numerically [27]. The idea is that the entropy of a knotted polymer may be maximized by the conformations in which knot is tightened within a short part of the chain, while the rest of the polymer fluctuates as a free unknotted loop. While the tendency to tighten the knot is quite strong for charged polymers [15], for neutral system it is governed by sub-linear in N terms of free energy and, therefore, is very sensitive to the details of structure and interactions. In this paper, we assumed that topological constraints are

delocalized along the polymer chain backbone. In the context of our work, this is justified for the following reasons. First, this issue is altogether irrelevant for the important case of the trivial knot, which is the first case considered in this paper. Second, for the non-trivial knots, it is necessary to understand the delocalized states in order to be able to push the question of knot segregation beyond the slip-link model of [14].

It should also be noted that in this paper we always assumed knots simple enough such that polymer chain is far from fully stretched state in the tube. The regime of such strong knotting requires special analysis [28].

To conclude, we presented the scaling theory determining the size of a polymer ring with quenched topology of a certain knot.

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